12. THE IDEAL GAS

The two extreme idealized thermodynamic systems are the ideal gas and the perfect crystal. In the first the arrangement of molecules (or atoms) is completely random, in the second it is perfectly ordered. The thermodynamic properties of an ideal gas are particularly instructive because of their relative simplicity. The simplest ideal gas is the monatomic ideal gas which will be discussed in the next chapter. Any real gas, monatomic or not, approximates the behavior of an ideal gas in the limit that $T \to \infty$ and $P \to 0$.

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12.1 The Fundamental Equation of the Ideal Gas in the Entropy Representation

Although thermodynamic theory does not depend on the existence of an explicit form of the fundamental equation (cf. § 3), it is, nevertheless, useful to learn how the theory applies when such a fundamental equation is available. The ideal gas presents us with the opportunity of studying the properties of a rather simple fundamental equation. The ideal rubber offers another such opportunity (cf. § 17.15).

The fundamental equation of an ideal gas cannot be derived within phenomenological thermodynamic theory. It can be obtained, however, in the entropy representation from a complete set of the equations of state (cf. § 12.3), and can also be derived with the help of classical statistical mechanics and quantum mechanics. Appendix 4 gives a short account of the derivation of the (molar) fundamental equation of the single-component ideal gas in the entropy representation. It leads to

$$s = s(u, v) = s_o + f(u) + R \ln \frac{v}{v_o} \quad (12.1)_1$$

where $R$ is the universal gas constant, $s = S/N$, $u = U/n$, $v = V/N$, and the subscript 'o' denotes a suitably chosen reference state. Equation $(12.1)_1$ contains no term which
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depends simultaneously on both \( u \) and \( v \) and thus satisfies the requirement for ideal behavior as formulated in § 11.2. The function \( f(u) \) is a function of \( u \) only. Its explicit form differs from gas to gas but it will always be such that \( f(u_0) = 0 \). Because \( f(u) \) is not known explicitly in general, Eq.(12.1) cannot be solved for the molar fundamental equation in the energy representation, \( u = u(s, v) \).

In terms of the mole number, \( N \), Eq.(12.1) becomes

\[
S = N \frac{S_o}{N_o} + N R \frac{U}{N} + N R \ln \frac{V N_o}{V_o N}
\]  

(12.1)_2

as the general form of the fundamental equation of a single-component ideal gas in the entropy representation. In the remainder of this chapter 'ideal gas' will refer to a single-component ideal gas unless otherwise stated.

12.2 The Equations of State of the Ideal Gas in the Entropy Representation

Because we have no explicit fundamental equation of the ideal gas in the energy representation, we derive the three equations of state of the ideal gas in the entropy representation. For the first equation we find

\[
\frac{1}{T} = \frac{\partial S}{\partial U} \bigg|_{V,N} = N \frac{d(f(U/N))}{dU} = \frac{d(f(u))}{du}
\]

(12.2)_1

from Eq.(3.11)_4.1. Although, in the absence of an explicit differentiable function of \( U \), the differentiation could only be indicated, Eq.(12.2)_1 shows that the internal energy depends—apart from the mole number, \( N \)—only on the temperature, \( T \). This exclusive dependence of the internal energy on the temperature is an important characteristic of the ideal gas and allows us to express the first equation of state of the ideal gas in the form

\[
\frac{1}{T} = c N R \frac{U}{U} = \frac{c R}{u}
\]

(12.2)_2

where \( c \) is a dimensionless constant (see the introduction to Chapter 13).

The second equation of state follows from Eq.(3.11)_4.1 as

\[
\frac{P}{T} = \frac{\partial S}{\partial V} \bigg|_{U,N} = \frac{NR}{V} = \frac{R}{v}
\]

(12.2)_3

This is commonly written as

\[
P V = NRT \quad \text{or} \quad P v = RT
\]

(12.2)_4
and has the same form for all ideal gases including the multicomponent ideal gas (cf. § 15.3). The second equation of state is sometimes referred to simply as THE equation of state of the ideal gas or THE ideal gas equation of state.

Introducing the equations \( U = cNRT \) and \( PV = NRT \) into \( H = U + PV \) it is seen at once that the enthalpy of an ideal gas also depends only on the temperature apart from the mole number, \( N \).

To derive the third equation of state we turn to Eq.(3.11)4.2. We find

\[
\frac{\mu}{T} = -\frac{\partial S}{\partial N}_{U,V} = -\frac{\partial}{\partial N} \left[ \frac{NS_o}{N_o} + N\frac{\partial(U/N)}{\partial N} + NR \ln \frac{VN_o}{V_oN} \right] \tag{12.2)_5}
\]

i.e.,

\[
\frac{\mu}{T} = -\frac{S_o}{N_o} - \frac{f(U/N)}{N} - N\frac{\partial(U/N)}{\partial N} - R \ln \frac{VN_o}{V_oN} + NR \frac{\partial \ln N}{\partial N}, \tag{12.2)_6}
\]

so that

\[
\frac{\mu}{T} = -\frac{S_o}{N_o} - \frac{f(U/N)}{N} + \frac{U}{N} \frac{\partial(U/N)}{\partial(U/N)} - R \ln \frac{VN_o}{V_oN} + R \tag{12.2)_7}
\]

or

\[
\frac{\mu}{T} = -s_o - f(u) + \frac{u}{T} - R \ln v/v_o + R. \tag{12.2)_8}
\]

Equation (12.2)_8 follows from (12.2)_7 because

\[
\frac{\partial(U/N)}{\partial(U/N)} = \frac{df(u)}{du}, \tag{12.2)_9}
\]

and this equals \( 1/T \) by Eq.(12.2)_1. Equations (12.2)_7 and (12.2)_8 represent the third equation of state of a single-component ideal gas.

12.3 Equivalence of the Complete Set of the Equations of State with the Fundamental Equation

In § 3.12 we asserted that the complete set of the equations of state is equivalent to the fundamental equation. Indeed, inserting Eqs.(12.2)_2, (12.2)_3, and (12.2)_8 into the molar form of the Euler equation, Eq.(3.10)_5, in the entropy representation,

\[
s = \frac{1}{T} u + \frac{P}{T} v - \frac{\mu}{T}, \tag{12.3}_1
\]

immediately reproduces the fundamental equation, Eq.(12.1)_1.
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The expectation that substitution of the equations

\[ T = \frac{u}{cR} \]  \hspace{1cm} (12.3)_{2}

\[ P = \frac{RT}{v} \]  \hspace{1cm} (12.3)_{3}

and

\[ \mu = -s_0T - Tf(u) + u - RT \ln v/v_o + RT \]  \hspace{1cm} (12.3)_{4}

into the molar form of the Euler equation in the energy representation,

\[ u = Ts - Pv + \mu, \]  \hspace{1cm} (12.3)_{5}

might lead to the fundamental equation in the energy representation, is not borne out.

In fact, doing so leads to

\[ T f(u) = us/cR - s_0T - RT \ln v/v_o \]  \hspace{1cm} (12.3)_{6}

and resubstitution of Eq. (12.3)_{2}, multiplication by \( T \), and rearranging leads to

\[ f(u) = s - s_0T - RT \ln v/v_o \]  \hspace{1cm} (12.3)_{7}

which we could have obtained simply by solving Eq. (12.2)_{1} for \( f(u) \).

12.4 Empirical Ideal Gas Laws

There are several historical empirical gas 'laws' that are commonly referred to under the name of their originators. Thus the dependence of the internal energy per mole, \( u \), on the temperature only, expressed by the first equation of state in the form \( u = cRT \) is sometimes referred to as Joule's Law. Several other such laws are seen to follow from the second equation of state. Boyle's Law claims that, for a given volume of an ideal gas at the same temperature, \( PV = \text{const} \), implying that the volume changes inversely as the pressure. The law first enunciated by Charles and later independently by Gay-Lussac states that at constant pressure a given volume of an ideal gas is directly proportional to the (absolute) temperature. This is expressed by \( V = NRT/P \). Finally, Avogadro's Law states that at the same temperature and pressure the molar volume of all ideal gases is the same. This follows from \( v = V/N = RT/P \).

12.5 The Primary Set of Partial Derivatives for an Ideal Gas

The second equation of state of an ideal gas leads to particularly simple expressions for the primary set of the second-order partial derivatives. Introducing \( V = NRT/P \) into Eqs. (10.2)_{2} and (10.2)_{3} yields the isobaric expansivity as

\[ \alpha_p = \frac{1}{V} \frac{\partial V}{\partial T} \bigg|_P = \frac{1}{T} \]  \hspace{1cm} (12.5)_{1}
and the isothermal compressibility as

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T = \frac{1}{P} \cdot \quad (12.5)_2$$

These two relations apply to any ideal gas, thus also to the monatomic and multicomponent ideal gases to be discussed in detail in Chapters 13 and 15.

The same cannot be said about the isochoric and the isobaric heat capacities of an ideal gas. Differentiation of the entropy, Eq.(12.1)_2, with respect to the temperature shows that the heat capacities of an ideal gas are functions of $f(u)$ and, therefore, generally, of the temperature. The monatomic ideal gas is an exception (see § 13). Since $f(u)$ differs from gas to gas for all other ideal gases, so also do $C_V(T)$ and $C_P(T)$. However, combining Eq.(10.3)_3, i.e., $c_P = c_V + T\alpha^2/\kappa_T$, with the equation of state, $Pv = RT$, gives the molar heat capacity difference of any ideal gas as

$$c_P(T) - c_V(T) = R, \quad (12.5)_3$$

which, for the monatomic ideal gas becomes simply $c_P - c_V = R$, and for any component of a multicomponent ideal gas takes the form $c_{P_i}(T) - c_{V_i}(T) = R$ (cf. § 15.4).

12.6 The Fundamental Equations of the Ideal Gas in Parametric Form

Since in an ideal gas $u$ depends on the temperature only, it is possible to express $f(u)$, and thus also the internal energy and the entropy of an ideal gas, in terms of the experimentally accessible molar heat capacities, $c_V(T)$ and $c_P(T)$. In either case the resulting expressions: $s = s(u, v)$ for the entropy, and $u = u(s, v)$ for the internal energy, then constitute two parametric equations for the fundamental equation. The latter could, in principle, be obtained in either the entropy or the energy representation from the parametric equations by elimination of $T$ between them. Because, however, the temperature dependence of the heat capacities is not known explicitly in general, this is possible only in special cases. The monatomic ideal gas (cf. § 13.1) represents such a special case.

While the parametric equations cannot be combined through the elimination of the temperature into fundamental equations in the energy or the entropy representations, it is possible to obtain fundamental equations from the parametric equations in the free energy and in the free enthalpy representations (cf. §§ 12.9 and 12.10). In these cases there is no need for the elimination of the temperature since it is a canonical variable in both these alternative representations.

12.7 The Parametric Fundamental Equations of the Ideal Gas in Terms of $c_V(T)$

We proceed to express the parametric equations of the single-component ideal gas in terms of the temperature dependence of the molar heat capacity at constant volume, $c_V(T)$. This can be determined experimentally and, in some cases, explicit expressions may be obtained from statistical mechanical considerations.

Because $u$ is a function of temperature only, Eq.(10.1)_4 becomes
\[ du = c_V(T) \, dT. \]  
(12.7)_1

and integration yields

\[ u = u_o + \int_{T_0}^{T} c_V(T') \, dT'. \]  
(12.7)_2

the molar form of the first of the sought-for parametric equations.

Substituting Eq.(12.7)_1 into the first equation of state, \( d\tilde{f}(u) = du/T \), and integrating using \( f(u_o) = 0 \), yields

\[ \tilde{f}(u) = \int_{T_0}^{T} \frac{c_V(T')}{T'} \, dT'. \]  
(12.7)_3

Inserting this into Eq.(12.1)_1 renders the second parametric equation as

\[ s = s_o + \int_{T_0}^{T} \frac{c_V(T')}{T'} \, dT' + R \ln \frac{V}{V_o}. \]  
(12.7)_4

Equations (12.7)_2 and (12.7)_4 are the molar parametric equations for a single-component ideal gas in terms of \( c_V(T) \), the molar heat capacity at constant volume.

12.8 The Parametric Fundamental Equations of the Ideal Gas in Terms of \( c_P(T) \)

The last three equations can be rewritten replacing \( c_V(T) \) by the experimentally more convenient \( c_P(T) \). Using Eq.(12.5)_3, i.e., \( c_V(T) = c_P(T) - R \), Eq.(12.6)_2 becomes

\[ u = u_o + \int_{T_0}^{T} c_P(T') \, dT' - R(T - T_o), \]  
(12.8)_1

Eq.(12.7)_3 yields

\[ f(u) = \int_{T_0}^{T} \frac{c_P(T')}{T'} \, dT' - R \ln T/T_o, \]  
(12.8)_2

and Eq.(12.7)_4 turns into
\[ s = s_0 + \int_{T_0}^{T} \frac{c_P(T')}{T'} \, dT' - R \ln \frac{T}{T_0} + R \ln \frac{v}{v_0} \quad (12.8)_3 \]

or

\[ s = s_0 + \int_{T_0}^{T} \frac{c_P(T')}{T'} \, dT' - R \ln \frac{P}{P_0} \quad (12.8)_4 \]

where \( P_0 = R T_0 / v_0 \). Equations (12.8)_1 with (12.8)_3 or with (12.8)_4 form alternative pairs of the molar parametric equations of the single-component ideal gas in terms of \( c_P(T) \), the molar heat capacity at constant pressure.

### 12.9 The Fundamental Equation of the Ideal Gas in the Free Energy Representation

To derive the expression for the fundamental equation of the ideal gas in the free energy representation, we first multiply the expressions for the molar parametric equations written in terms of the heat capacity at constant volume, \( c_V(T) \), by the number of moles, \( N \). This leads to

\[ U = N \frac{U_0}{N_0} + N \int_{T_0}^{T} c_V(T') \, dT' \quad (12.9)_1 \]

from Eq.(12.7)_2, and to

\[ S = N \frac{S_0}{N_0} + N \int_{T_0}^{T} \frac{c_V(T')}{T'} \, dT' + N R \ln \frac{v}{v_0} \quad (12.9)_2 \]

from Eq.(12.7)_4. Combining these according to \( F = U - TS \) gives

\[ F = \frac{N}{N_0} F_0 + N \int_{T_0}^{T} \frac{T' - T}{T'} c_V(T') \, dT' - N R T \ln \frac{v}{v_0} \quad (12.9)_3 \]

with \( F_0 = U_0 - T S_0 \), as the fundamental equation of the ideal gas in the free energy representation.

### 12.10 The Fundamental Equation of the Ideal Gas in the Free Enthalpy Representation

To obtain the fundamental equation of the ideal gas in the free enthalpy representation we use the parametric equations written in terms of the heat capacity at constant pressure, \( c_P(T) \), since we need the pressure as another canonical variable in this case. By multiplying with the number of moles, \( N \), we obtain
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\[
U = N \frac{U_0}{N_o} + N \int_{T_0}^{T} c_p(T') \, dT' - NR(T - T_0) \quad (12.10)_1
\]

from Eq. (12.8)_1, and

\[
S = N \frac{S_0}{N_o} + N \int_{T_0}^{T} \frac{c_p(T')}{T'} \, dT' - NR \ln P/P_o - T_0 \quad (12.10)_2
\]

from Eq. (12.8)_4. Using both \( G = U - TS + PV \) and \( PV = NRT \) yields

\[
G = N \frac{G_0}{N_o} + N \int_{T_0}^{T} \frac{T' - T}{T'} \, c_p(T') \, dT' + NRT \ln P/P_o \quad (12.10)_3
\]

with \( G_0 = U_0 - TS_0 + P_0V_0 \), as the fundamental equation of the ideal gas in the free enthalpy representation.

12.1.1 The Gibbs-Duhem Equation of the Ideal Gas in Terms of \( c_p(T) \)

Multiplication of the third equation of state, Eq. (12.2)_8, by \( T \) yields

\[
\# = - T_0u_0 - T_0u(T) + u - RT \ln v/v_0 + RT \quad (12.11)_1
\]

With the help of Eqs. (12.8)_1 and (12.8)_2 and the use of \( PV = RT \) this becomes

\[
\mu = \mu_0(T) + RT \ln P/P_o \quad (12.11)_2
\]

where

\[
\mu_0(T) = u_0 - Ts_0 + RT_0 + \int_{T_0}^{T} \frac{T' - T}{T'} \, c_p(T') \, dT' \quad (12.11)_3
\]

or, alternatively,

\[
\mu_0(T) = u_0 - Ts_0 + RT - RT \ln T/T_0 + \int_{T_0}^{T} \frac{T' - T}{T'} \, c_v(T') \, dT'. \quad (12.11)_4
\]

The function \( \mu_0(T) \) is the standard chemical potential at the temperature \( T \) and the standard (reference) pressure \( P_0 \). The zero subscript in \( \mu_0(T) \) refers to this pressure. Thus \( \mu_0(T) \) is standard with respect to a standard pressure but it is a function of temperature.

Equation (12.11)_2 with either (12.11)_3 or (12.11)_4 provides a functional relation between the intensive parameters \( T, P, \) and \( \mu \). They thus together represent the integrated
form of the Gibbs-Duhem equation of the ideal gas in terms of the molar heat capacities at constant pressure or constant volume. Behavior in accordance with Eq. (12.11) constitutes a sufficient condition for the ideal behavior of a gas.